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Reduction and Metathesis Activity of MoO_3/Al_2O_3 Catalysts

II. The Activation of MoO_3/Al_2O_3 Catalysts

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MoO_3/Al_2O_3 catalysts (0.5–13 wt% MoO_3) were activated for the metathesis of propene by thermal treatment in flowing inert gas and by reduction in H_2 (reaction conditions: 473 K, 0.1 MPa). Temperatures between 900 and 1140 K were applied for the activation of the catalysts in inert atmosphere. The activity of the supported Mo (molecules s^{-1} Mo^{-1}) increased with decreasing MoO_3 content, which is opposite to the well-known trends for the reducibility of Mo(VI)/Al_2O_3. The kinetic reaction order of the propene metathesis was found to be 0.8 at 473 K. The apparent activation energy was 30–37 kJ/mole, with a slight decrease at increasing MoO_3 content. The response of the activity to the extent of reduction was investigated at different reduction temperatures and MoO_3 contents. From these observations and the results of the thermal activation study, it has been concluded that the active sites of metathesis can be formed from both Mo(VI) and Mo(IV) precursors. These precursors coexist on reduced surfaces, while the activity attained after thermal activation in inert gas is due exclusively to sites originating from Mo(VI) species. Other Mo states (Mo(V), Mo(II), and Mo(0)) do not contribute to the metathesis activity.

INTRODUCTION

In the recent literature, the development of the metathesis activity of supported molybdena and tungsten oxide has been ascribed to active sites originating from surface compounds in which the metal is in the +4 oxidation state. This conclusion has been drawn most convincingly from investigations with model catalysts prepared via the fixation of organometallic complexes (*1*, *2*) and with photoreduced Mo/SiO_2 (*3*). Several possible pathways for the formation of the active carbene sites from Mo(IV) (W(IV)) precursor species have been proposed (*2*, *4*). With the model catalysts mentioned above, a route involving the abstraction of a vinyl hydrogen by the central Mo ion has been substantiated by isotopic methods (*2*, *5*).

For more conventional catalysts the situation is less clear. Certainly, the reduction of the catalyst (with subsequent removal of adsorbed hydrogen (*6*)) has been frequently found to favor the metathesis reaction (*6*–*9*), and a relation between the reducibility of the hexavalent Mo (or W) ion on a support surface and the metathesis activity of the corresponding catalyst has been established (*10*, *11*). To a considerable extent, this relation is based on the observation that alumina-supported catalysts with a small metal oxide content, the reducibility of which is very low, exhibited inferior metathesis activities (*11*).

On the other hand, some metathesis activity is also often found with unreduced catalysts (*6*, *8*, *9*) and there is a report on a situation where no influence of the reduction degree on the metathesis activity was detected (*12*). For Mo/TiO_2 systems, the average oxidation number of the most ac-

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tive surfaces was found to be considerably higher than +4; more extensive reduction caused a drastic loss of activity (*13*). This evidence may suggest the existence of a second active site precursor, the oxidation state of which is higher than +4. In the past, Mo(V) species were repeatedly considered to be involved in the metathesis sites (*9, 14*). Mo(VI) was proposed to be the active site precursor in an activation process where the metathesis reaction is initiated by the treatment of an oxidized MoO_3/Al_2O_3 catalyst with olefin at room temperature (*15a*). However, in a subsequent paper the same authors considered a slight reduction of the surface, which is indicated by the emergence of a Mo(V) EPR signal, to be also essential for the activation (*15b*). In the remaining literature, the hexavalent state has been almost completely discarded from the discussion (except for photocatalytic metathesis processes (*16*, 17)) although it is assumed to be relevant in the precursors of homogeneous metathesis catalysts (*18*, *19*) and its potential role in the formation of active sites has been proposed on the basis of theoretical studies (*20*).

In our former work on the metathesis activity of alumina-supported WO_3 we found that on surfaces activated by thermal treatment in inert gas the active sites are formed from precursor structures containing tungsten in the +6 state (*21*). It was shown that this does not contradict the literature that proves the relevance of tetravalent active site precursors. Indeed, reduction of samples under conditions that allow the detection of W(IV) on the surface by XPS led to the development of an activity contribution in excess of the level provided by activation in inert gas (*21*, *22*). The aim of the study reported in this paper was to supply analogous evidence for MoO_3/Al_2O_3 catalysts.

In this investigation we were faced with a situation different from that in the tungsten systems, as the reduction of MoO_3/Al_2O_3 catalysts is known to start at relatively low temperatures yielding a variety of reduced Mo states. In part I of this work (*23*), an XPS investigation of the surface of MoO_3/Al_2O_3 catalysts after treatments normally used to activate them for the metathesis reaction has been reported. It was found that during thermal treatment in flowing inert gas, part of Mo(VI) initially present on the surface undergoes reduction to Mo(V). The XPS spectra suggested a slightly increasing extent of this reduction when the MoO_3 content increased from 4 to 13 wt%. After reduction in hydrogen, the surface of MoO_3/Al_2O_3 catalysts was shown to contain Mo(VI), Mo(V), Mo(IV), Mo(II), and, above 900 K, Mo(0). For a wide range of reduction conditions, distributions of these Mo states that deviate from those known from the literature due to the application of a recently derived modified relation between Mo binding energies and oxidation states (*24*) were determined. Thermal treatment of a reduced surface in flowing inert gas at 973 K led to a partial reoxidation of the surface, probably by residual OH groups, which was not reversed by readsorption of hydrogen at 823 K.

EXPERIMENTAL

1. Materials. The catalysts (0.5–13 wt% MoO_3/Al_2O_3) were identical with those used in part I (*23*). They were prepared by impregnation of γ-Al_2O_3 (Leuna-Werke, Leuna, Germany, BET surface area ≈260 m^2/g) with solutions of MoO_3 in NH_4OH (pH ≈ 8) by the incipient wetness technique. After drying at 400 K and calcination at 823 K they were stored in air prior to use. In Table 1, the MoO_3 content of these catalysts is resumed and the code used to de-

TABLE 1

MoO_3/Al_2O_3 Catalysts Investigated: MoO_3 Contents and Sample Codes

Catalyst	Mo0.5	Mo1	Mo2	Mo4	Mo7	Mo13
wt% MoO_3[a]	0.45	1.1	1.8	4.5	7.4	12.9

[a] Determined by electron microprobe analysis.

note the samples is illustrated. For further information, the reader is referred to part I of this research (*23*). The highest MoO_3 content employed is well below the monolayer capacity of the alumina, which is $\approx$20 wt% MoO_3.

H_2, Ar, and propene from cylinders were deoxygenated over MnO/Al_2O_3, dried over $Mg(ClO_4)_2$, and repurified by an oxygen trap (MnO/Al_2O_3) at the entrance of the reactor. The propene (Sächsische Olefinwerke Böhlen, Germany) contained 0.07 vol% propane and 0.03 vol% ethene. The air used for the regeneration of the catalysts between the catalytic runs was dried over a Zeosorb 4A molecular sieve.

2. *Reaction procedure.* The propene metathesis was studied in a conventional flow reactor at atmospheric pressure and at 473 K if not stated otherwise ("standard conditions"). The reaction procedure has been outlined in detail elsewhere (*21*). Prior to every run, the catalysts (0.15–1 g, particle size 0.4–0.8 mm) were recalcined (or regenerated) in air at 823 K for 2 h before they were heated in Ar (6 liters/h) to the temperature of activation. When the activation was to be performed in an inert atmosphere the samples were cooled to the reaction temperature after 2 h of exposure to flowing Ar at the activation temperature. Subsequently, propene (undiluted if not stated otherwise) was charged. As in the case of WO_3/Al_2O_3 catalysts (*21*), neither an induction period (first conversion measurement after $\approx$5 min time-on-stream) nor any deactivation in the course of 3 h time-on-stream could be observed. Normally, the effluent was sampled after 30 min time-on-stream.

In the activation with hydrogen, fresh portions of catalyst recalcined in air at 823 K for 2 h were heated in Ar to the reduction temperature and reduced in flowing hydrogen. After the reduction, hydrogen retained on the surface had to be stripped off from the catalyst ((*6*), cf. Results section). Owing to limited vacuum facilities in one of the participating laboratories this stripping was performed by treating the samples in flowing Ar for 2 h at 973 K (in some cases 923 K). Subsequently, the catalysts were cooled to the reaction temperature of 473 K in the Ar flow, a propene/N_2 mixture ($\approx$5 vol% propene) was charged, and the effluent was analyzed after 30 min time-on-stream. In series with varying reduction time every reduction period was investigated with a fresh sample.

The reaction products were analyzed by GC (50 m × 0.25 mm polydimethylsiloxane-fused silica capillary column at room temperature). Testing the CO_2 content of the effluent air during the regeneration of the catalysts showed that the quantity of the carbonaceous residue corresponded to a propene conversion in the order of 0.001 (0.1%). The carbonaceous residue has, therefore, not been analyzed in these experiments.

For reasons that have not yet been fully elucidated, the reproducibility of metathesis activities measured with MoO_3/Al_2O_3 catalysts after activation in an inert atmosphere was much lower than that with WO_3/Al_2O_3 catalysts. Sometimes series were obtained differing from each other in the activity level by 30–40%, but having the same graduation between the different catalysts. An example is included in Fig. 3. With the Mo13 catalyst, these effects were found to be most pronounced and, eventually, the catalyst failed to exhibit any metathesis activity. We believe that the reason for this trouble, which affects the absolute activities but not the trends discussed in this paper, is that molybdena-based metathesis catalysts are possibly even more easily poisoned by oxygen traces in the gases or mobile oxygen on the surface than WO_3/Al_2O_3 catalysts (*21*). The reason why highly loaded MoO_3/Al_2O_3 catalysts suffer from this to a larger extent may be that the species capable of forming active sites constitute a particularly small fraction of the Mo component in them (vide infra).

3. *Presentation of metathesis data.* The metathesis reaction proved to be highly selective under our reaction conditions. At a

reaction temperature of 473 K, products other than C_2–C_4 olefins (propane, C_5 olefins) amounted to less than 0.2% of the total of hydrocarbons and even at reaction temperatures up to 673 K these consecutive or by-products could be neglected. The butene–ethene ratio was averaged over 130 runs at 0.99 ± 0.01. The ratio between butene-(1) and the sum of *cis*- and *trans*-butene-(2) was not at equilibrium at 473 K (0.02–0.08 compared with 0.12, as estimated from data in (*25*)). Below 423 K, butene-(1) was not observed in most of the runs. The equilibrium of butene isomerization was attained at 573 K (see also (*21*)).

In the following, activities are compared using conversions x (or $100x$, %) for constant volumetric flow rates per kilogram of catalyst (b) or an initial reaction rate referred to the Mo content of the sample. The latter, which has a unit of "mole propene converted per second and mole Mo," or s^{-1}, is equivalent to a turnover frequency (TOF) provided that all of the molybdenum present takes part in the reaction. Although this is certainly not the case, this "initial reaction rate per Mo" will be abbreviated as a TOF throughout this paper for the sake of brevity. The initial rates were evaluated using the kinetic rate law observed (see Eq. (1), $m = q = 0.8$) for extrapolation to differential conversions.

The thermal activation of the catalysts with low MoO_3 content causes a considerable loss of the internal support surface area (see Table 1 of part I (*23*)). In the case of analogous WO_3/Al_2O_3 catalysts (*21*), this loss of surface area was not relevant to the evaluation of the kinetic data as the tungstate phase remained segregated during the thermal degradation of the pore system (*26*). For molybdena catalysts an evidence like this is not available. High calcination temperatures may lead to the formation of $Al_2(MoO_4)_3$ (*27*) or to Mo losses (*28*). Preliminary XPS results from such samples indicate a decrease of the relative Mo intensity (*29*); i.e., the main effect of high-temperature calcination should be a decrease in the amount of accessible Mo in these cases. Because a consideration of this effect would not alter the conclusions drawn in this paper, the activity data were referred to the Mo contents of the samples determined after calcination at 823 K (Table 1).

RESULTS

Thermal Activation in Ar

1. Optimum activation conditions. In Fig. 1, the influence of the activation temperature on the propene conversion measured under standard reaction conditions is presented. The volumetric flow rates of propene are constant for each sample and are given in the legend. It can be seen that an increase of the activation temperature drastically improves the metathesis activity, especially at low Mo content. While this is quite similar to the observations made with WO_3/Al_2O_3 catalysts, there is no parallel in the behavior of the corresponding tungsten systems (*21*) with regard to the significant loss of activity upon the applica-

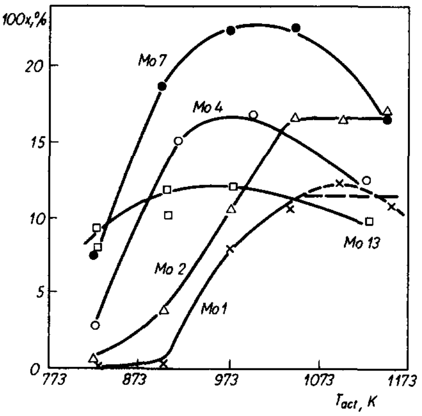


Fig. 1. Activation of MoO_3/Al_2O_3 catalysts in flowing Ar: Dependence of the activity on the activation temperature. Reaction temperature 473 K; P = 0.1 MPa; feed gas, 100 vol% propene, activity given as propene conversion at constant volumetric flow rate per kilogram catalyst: (X) Mo1, $b \simeq 40\ m^3\ kg^{-1}\ h^{-1}$; (△) Mo2, $b \simeq 50\ m^3\ kg^{-1}\ h^{-1}$; (○) Mo4, $b \simeq 90\ m^3\ kg^{-1}\ h^{-1}$; (●) Mo7, $b \simeq 90\ m^3\ kg^{-1}\ h^{-1}$; (□) Mo13 $b \simeq 60\ m^3\ kg^{-1}\ h^{-1}$.

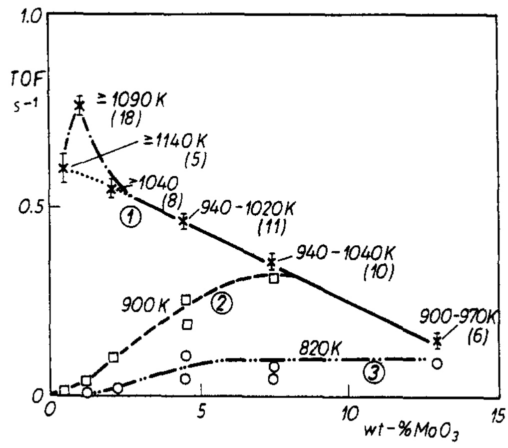


Fig. 2. Activation of MoO_3/Al_2O_3 catalysts in flowing Ar: Dependence of the turnover frequency (TOF) on the MoO_3 content. Reaction conditions as in Fig. 1. Feed gas, 5–100 vol% propene in N_2. Curves: (1) maximum activity, range of activation temperatures, and number of runs inserted for each temperature (vertical bars indicate standard deviation); (2) activation at 900 K; (3) activation at 820 K. Vertical bars:

$$s_m = [\Sigma_j (\overline{TOF} - (TOF)_j)^2/(n(n - 1))]^{1/2}.$$

For the evaluation of the TOF, which is related to the whole of Mo present, see Section 3 under Experimental.

tion of too high temperatures to Mo4, Mo7, and Mo13. For these molybdena catalysts, an optimum activation effect is obtained in a temperature range that only slightly depends on the Mo content (see also Fig. 2).

For catalysts with MoO_3 contents below 4 wt%, temperatures above 1000 K are required to develop the metathesis activity of the surfaces. Obviously, activation at too low temperatures was the reason why other authors have considered these catalysts to be practically inactive (*11*). In the range of low Mo content, an activity loss resulting from too high pretreatment temperatures could not be unambiguously stated. These catalysts reach their full activity at activation temperatures that are already deleterious for catalysts with higher Mo content.

In Fig. 2, the TOFs (referred to the total of Mo) obtained under standard reaction conditions after thermal activation in flowing Ar are plotted versus the MoO_3 content of the catalysts. The range of activation temperatures from which the data have been summarized and the number of runs included are also given. The vertical bars indicate standard deviations of the mean values (see formula given in the legend). The results resemble the earlier findings with WO_3/Al_2O_3 catalysts (*21*): The TOF drops with increasing MoO_3 content. Insufficient activation temperatures (curves 2 and 3) result in a reverse tendency and feign a correlation with the reduciblity of the catalyst.

2. *Kinetic aspects.* The reaction order of propene has been investigated for the fully activated state by applying propene, which was diluted by N_2 to different initial concentrations (down to ≈5 vol%), at a constant feed rate. If the reaction rate r (mole kg^{-1} h^{-1}) can be expressed as

$$r = k_1(c_{0,P}(1 - x))^m - k_{-1}(0.5\, c_{0,P}\, x)^q, \quad (1)$$

where

k_1, k_{-1}—rate constants of the metathesis and the reverse reaction, units depending on m and q,

m, q—reaction orders of metathesis and reverse reaction,

$c_{0,P}$—initial propene concentration, *mole* m^{-3},

x—conversion $((c_{0,P} - c_P)/c_{0,P})$,

a logarithmic plot of the reaction rate versus the propene concentration for small conversions should produce straight lines, from which the reaction order m may be calculated. Figure 3 shows, with a somewhat extended range of conversions ($x \leq 0.12$), that this is indeed the case, i.e., that the kinetics of the metathesis can be described by a power law for our catalysts and the conditions employed. However, in contrast to the results obtained with WO_3/Al_2O_3 (*21*), the reaction order deviates from 1 and it is ≈0.8 in all cases. The rate constants estimated from these plots are indicated by arrows in Fig. 3. An example of

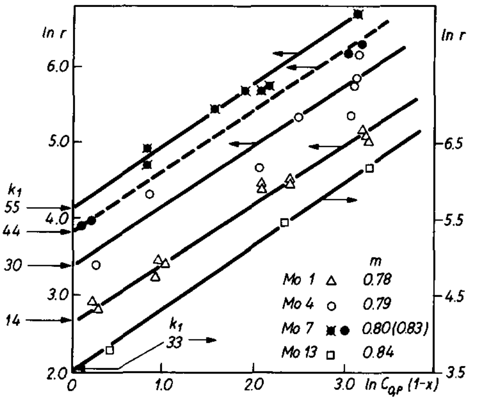


Fig. 3. Determination of the propene reaction order m for activated MoO_3/Al_2O_3 catalysts. Activation as indicated in Fig. 2, curve 1; for mathematical formalism see text. Reaction temperature, 473 K; $P = 0.1$ MPa; feed gas, 5–100 vol% propene in N_2; conversion, $x \leq 0.12$. (△) Mo1, $b \simeq 60$ m^3 kg^{-1} h^{-1}; (○) Mo4, $b \simeq 380$ m^3 kg^{-1} h^{-1}; (●, ■) Mo7, $b \simeq 280$ m^3 kg^{-1} h^{-1}; (□) Mo13, $b \simeq 250$ m^3 kg^{-1} h^{-1}.

series with differing basis activity (see Experimental) is also given in this figure (Mo7).

Applying the kinetic description of the equilibrium

$$k_1(c_{0,P}\,(1 - x_\infty))^m = k_{-1}\,(0.5\,c_{0,P}\,x_\infty)^q$$

and introducing the volumetric flow rate b, Eq. (1) may be transformed to

$$r\left(= c_{0,P}\,\frac{dx}{d(b^{-1})}\right) = \frac{k_1\,c_{0,P}^m}{x_\infty^q}\,(x^q(1 - x_\infty)^m - x_\infty^q(1 - x)^m),$$

which yields by integration

$$I(x) = \int_0^x \frac{dx}{x_\infty^q(1 - x)^m - x^q(1 - x_\infty)^m} = k_1\,b^{-1}\,c_{0,P}{}^{m-1}\,x_\infty^{-q}. \quad (2)$$

In Eq. (2), the integral $I(x)$ was evaluated numerically for several q ($0.6 \leq q \leq 1.0$), applying values for x_∞ estimated from thermodynamic data as described in *(21)* ($x_\infty = 0.4$ for 473 K; for other temperatures see Fig. 4). These data may be used in several ways. First, the experimental propene conversions may be employed, together with the rate constants k_1 drawn from Fig. 3 (for $x \leq 0.12$), to estimate the order of the reverse reaction. This is, however, a rather rough estimation as meaningful results may be expected only at high conversions (e.g., $x \geq 0.2$), where, on the other hand, the quality of the estimate of x_∞ becomes critical. Within the limits of series with identical basis activity (see, e.g., Fig. 3—the two series for Mo7), q was strongly scattering but fell into the range of 0.65–0.95. The value of $q = 0.8$ was used for further calculations.

In these calculations, the rate constant k_1 was computed from the conversion data and the integral $I(x;\ m = q = 0.8)$ for the whole range of conversions ($0.03 < x < 0.25$) and initial propene concentrations (5–100 vol%), including runs with varied reaction temperatures (vide infra). It was found that q has only a minor influence on the k_1 values: Thus, at a conversion of $x \simeq 0.25$ ($x_\infty = 0.4$), k_1 drops only by $\simeq$10% when q is increased from 0.6 to 0.8. The more relevant values of k_1, which are also the basis of Fig. 2, are given in Table 2.

In Fig. 4, the temperature dependence of

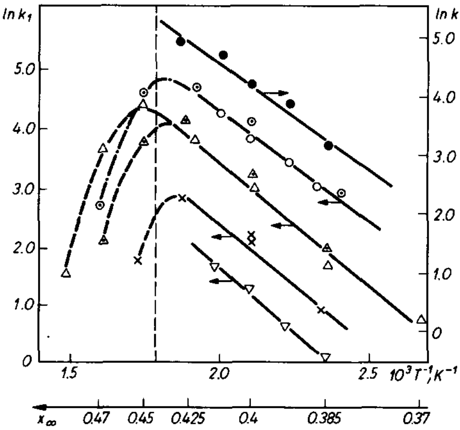


Fig. 4. Temperature dependence of the rate constant of the propene metathesis over MoO_3/Al_2O_3 catalysts. $P = 0.1$ MPa; feed gas, 100 vol% propene; conversion, $0.03 \leq x \leq 0.25$; k_1 given in mole$^{0.2}$ m$^{2.4}$ kg^{-1} h^{-1}. (▽) Mo0.5; (X) Mo1; (△, ◬) Mo2, different series; (○, ⊙) Mo4, different series; (●) Mo7; (x_∞) equilibrium conversion used for the evaluation of k_1.

TABLE 2

Rate Constants, k_1, Apparent Activation Energies, E_a, and Reaction Rates at 473 K, r_{473}, of the Propene Metathesis over MoO_3/Al_2O_3 Catalysts

Catalysts	T_{act} (K)	k_1 at 473 K ($mole^{0.2}$ $m^{2.4}$ kg^{-1} h^{-1})[a]	E_a (373–523 K) (kJ/mole)	r_{473}[b] (mole kg^{-1} h^{-1})
Mo0.5	1143	4.9	37.1	66
Mo1	1093	15.7	34.7	203
Mo2	1043–1093	18.6	35.0	250
Mo4	973–1043	39.0	32.2	525
Mo7	923–973	46.5	30.2	625
Mo13	898–973	36.2	—	490

[a] Unit of the rate constant in Eq. (1) for a reaction order $m = 0.8$.

[b] At $P = 0.1$ MPa, feed gas, 100 vol% propene.

the metathesis rate constant is presented. The runs were performed as described previously (*21*); i.e., at a constant feed rate a series of reaction product samples was withdrawn while the catalyst underwent a specified temperature program with a 15-min isothermal period at every reaction temperature selected. It was assumed that the kinetics do not change in the temperature range around 473 K.

The ln k_1 vs T^{-1} relationship is linear between 370 and 530 K. At higher temperatures the rate constants go through a maximum and then decrease drastically. As shown in the figure, the runs were not reproducible in the region of this decrease although they were in the 370–530 K range. The reason for this is not known. At comparable temperatures the activities of the MoO_3/Al_2O_3 catalysts are in the same order of magnitude as those of WO_3/Al_2O_3 catalysts with the same metal oxide loading. The apparent activation energies, which are compiled in Table 2, exhibit only a very slight decrease with increasing MoO_3 content, which is in contrast to the pronounced effect of the metal oxide content observed with WO_3/Al_2O_3 catalysts (*21*).

Activation by Reduction in Hydrogen

It has been reported in the literature that reduced MoO_3/Al_2O_3 catalysts become active for metathesis only after hydrogen retained by the surface is removed by an evacuation at the temperature of reduction (*6*). In our work, a thermal treatment in inert gas was employed to desorb hydrogen from the catalyst. Table 3 shows that a desorption temperature of 923 K is sufficient to bring out the activity of the reduced surface (runs 2, 3). As reported in (*6*), flushing the activated catalyst with hydrogen at

TABLE 3

Influence of Adsorbed Hydrogen on the Metathesis Activity of a Reduced MoO_3/Al_2O_3 Catalyst

Run	Pretreatment	Conversion (100x) (%)
1	2 h Ar, 923 K	12
2	2 h Ar, 923 K + 30 min H_2, 773 K	1
3	2 h Ar, 923 K + 30 min H_2, 773 K + 2h Ar, 923 K	16
4	2 h Ar, 923 K + 30 min H_2, 773 K + 2h Ar, 923 K + 15 min H_2, 298 K	16
5	2 h Ar, 923 K + 30 min H_2, 773 K + 2h Ar, 923 K + 5 min H_2, 773 K	1

Note. Sample, Mo7. Volumetric flow rate per kg of catalyst, 128 m^3 kg^{-1} h^{-1}; reaction temperature, 473 K; feed gas, 10 vol% propene in N_2.

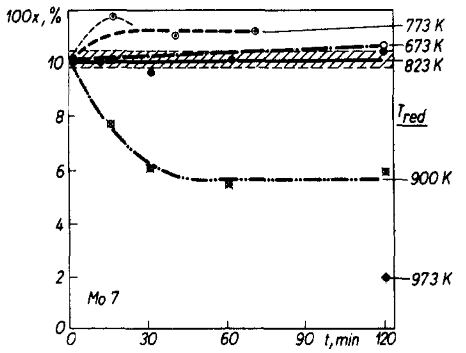


Fig. 5. Activation of a 7 wt% MoO_3/Al_2O_3 catalysts for propene metathesis by reduction in H_2 at different temperatures (including a subsequent Ar treatment for 2 h at 973 K for desorption of hydrogen; see text). Reaction temperature, 473 K; $P = 0.1$ MPa; activity given as propene conversion at constant volumetric flow rate per kg of catalyst (107 $m^3\ kg^{-1}\ h^{-1}$); feed gas, 5.3 vol% propene in N_2. ▨, activity obtained after activation in inert gas (T_{act}: 973 K); ‒‒○‒‒, activation in H_2 at 673 K; ‒‒⊙‒‒, activation in H_2 at 773 K; —●—, activation in H_2 at 823 K; ‒‒⊗‒‒, activation in H_2 at 900 K; ⊕, activation in H_2 at 973 K.

room temperature does not impair the activity (run 4), while a short contact of the surface with H_2 at 773 K (run 5) quenches the activity effectively. It should be noted that the activity of a catalyst containing hydrogen adsorbed at high temperature is far below the level obtained by a mere thermal treatment in inert gas.

The response of the metathesis activity to the conditions of catalyst reduction depended on the Mo content. Figure 5 shows the development of the metathesis activity with increasing time of reduction at different reduction temperatures for the catalyst Mo7. The activity, measured under standard reaction conditions (cf. Experimental), is reported as propene conversion at constant volumetric flow rate. The shaded region indicates the activity obtained by thermal activation in Ar with typical margins of experimental error. Depending on the reduction temperature, the effect of the hydrogen treatment on the metathesis activity is different. Below 823 K, the reduction has a slightly promoting effect, but above 823 K significant losses in activity are obvious. At a reduction temperature of 823 K, the metathesis activity did not depend on the reduction time at all. With Mo4, the same response of the metathesis activity to the reduction conditions was found. This response is probably typical for catalysts with low MoO_3 content (cf. Discussion).

At a high MoO_3 content (Mo13, Fig. 6) the activating effect of the hydrogen treatment becomes more pronounced. With increasing reduction time, activity maxima are found at reduction temperatures of 773 and 823 K. While at the latter temperature the maximum seems to be at a reduction time of even less than 15 min, which was the shortest period studied, the 773 K curve shows a delayed increase in activity with increasing reduction time. This effect has been confirmed at the reduction temperature of 673 K. At this temperature, the activity increased only after a period of 40 min, in which no significant changes of the propene conversion were found. By analogy to Mo7, reduction of Mo13 at temperatures above 823 K leads to a loss of metathesis activity.

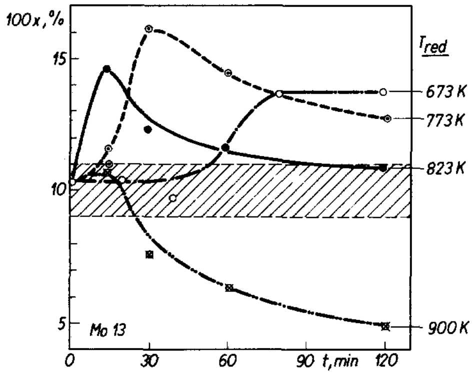


Fig. 6. Activation of a 13 wt% MoO_3/Al_2O_3 catalyst for propene metathesis by reduction H_2 at different temperatures (including a subsequent Ar treatment for 2 h at 973 K for desorption of hydrogen; see text). Reaction temperature, 473 K; $P = 0.1$ MPa; activity given as propene conversion at constant volumetric flow rate per kg of catalyst (71 $m^3\ kg^{-1}\ h^{-1}$), feed gas, 4.5 vol% propene in N_2. For meaning of symbols see Fig. 5 legend.

DISCUSSION

1. Thermal activation in Ar. The activation behavior of MoO_3/Al_2O_3 catalysts and the metathesis kinetics over them exhibit analogies as well as some characteristic differences to the corresponding tungsten catalysts. In both systems thermal treatment in flowing inert gas is an effective activation procedure. Different from the tungsten system, Mo catalysts do not tolerate temperatures in excess of an optimum value. In both cases the catalysts with the lowest metal oxide content require the highest activation temperatures. The TOF (related to the whole of the metal present) increases with decreasing metal oxide loading thus being highest for the catalysts with the lowest reducibility (*22*, *23*, *27*).

The kinetic reaction order of the propene metathesis is 1 over WO_3/Al_2O_3 at 573 K (*21*), but 0.8 for MoO_3/Al_2O_3 at 473 K. The proposal that the reaction of an adsorbed propene molecule with a carbene site is rate-determining (*2*) may explain both values when different exponents are used in the Freundlich equation to describe the propene adsorption (1 for W at 573 K, 1.25 for Mo at 473 K). The Freundlich exponent of 2 reported in (*2*) for fixed Mo/Al_2O_3 catalysts at 273 K suggests that there may be common reaction kinetics for all three systems, the differences being due to the temperature dependence of the adsorption exponent. More work is, however, necessary to clarify this point. The latter proposal contradicts to some extent the assumptions according to which the activation energies have been calculated. The tendencies observed with the activation energies (decrease with increasing metal oxide content with W, only slight variations with Mo) should not be affected by this.

The analogies described, in particular the inverse tendencies of reducibility and TOF in both cases, suggest analogous conclusions concerning the valence and the structure of the active site precursor in both MoO_3/Al_2O_3 and WO_3/Al_2O_3 catalysts (*21*). This would mean that a hexavalent, probably tetrahedral precursor species is responsible for the activity of thermally activated MoO_3/Al_2O_3 catalysts. The whole of the material contains, however, some ambiguities that must be discussed in more detail.

Thus, Mo(V) is present on the active surface to an extent considerably exceeding that of W(V) on active WO_3/Al_2O_3 surfaces and, unlike in the case of tungsten (*30*), the analysis of the Mo(V) content turned out not to be straightforward and yielded large differences between the results of EPR and XPS (cf. part I (*23*)). It should be noted, however, that with samples treated in Ar at 973 K the moderate decrease of the TOF with increasing MoO_3 content (see Fig. 2) does not correlate with the tendency of slightly increasing percentage of Mo(V) that can be derived from the XPS spectra and is considered by the authors to be correct (*23*). Additional evidence for the irrelevance of the Mo(V) state for the metathesis reaction is given below.

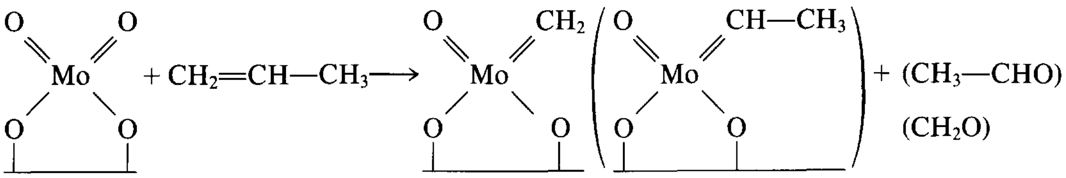
As to the coordination of the Mo(VI) precursor species, we must refer to a literature that is much more contradictory than in the case of tungsten. Many authors favor the view that tetrahedral molybdate structures prevail at low metal oxide content, while patches of octahedral polymeric molybdate with only a part of the Mo ions interacting with the support coexist with a minor amount of the more tightly bound tetrahedral entities at higher loadings (*27*, *31–33*). On the other hand, there are reports claiming the predominance of octahedral molybdates even at low MoO_3 content (*34–36*). The Mo_O/Mo_T ratio may further depend on the preparation conditions. From this point of view, we expected a high contribution of tetrahedral molybdate entities at MoO_3 contents ≤ 2 wt% despite our rather unfavorable impregnation technique as the pH was high ($\simeq 8$) and the solute concentration low (*32*, *37*, *38*). At MoO_3 contents >7 wt% clustering of the molybdate phase, which implies an increasing role of octahedral structures, has been detected even in the rather insensitive XPS intensities (see part I (*23*)).

Unfortunately, powerful methods of structural investigation such as EXAFS or laser Raman spectroscopy, were not previously available to us. The UV–VIS spectra of the catalysts under discussion exhibit a main absorbance maximum at 215–245 nm shifting from 230–245 nm (Mo13) to 215–220 nm (Mo2, Mo1) with decreasing MoO_3 content, and a shoulder at 270–290 nm (*39*). The ratio between these two absorptions does not appear to change significantly with decreasing MoO_3 content. According to the current views on the assignment of the charge-transfer bands in this system, summarized in (*40*), we must consider the existence of both isolated tetrahedral and clustered octahedral Mo species even at low MoO_3 content. It has been questioned, however, whether the UV–VIS technique is really able to distinguish between the tetrahedral or octahedral coordination of Mo oxo species (*40*).

The view that the Mo(VI) precursor possesses tetrahedral coordination therefore needs further substantiation although it is supported by the analogy with the WO_3/Al_2O_3 system (*21*) and with tetrahedral Mo(VI) complexes being precatalysts in homogeneous metathesis reactions (*18*). The assumption that tetrahedral molybdate structures may occupy only a minute fraction of the sites on the alumina surface, thus forming a small minority of species with almost equal interactions with the support at increasing MoO_3 content, could explain an increased susceptibility of MoO_3/Al_2O_3 catalysts to poisoning (cf. Experimental) as well as the trends observed with the activation energies: The more pronounced variation of the latter in the case of tungsten would then reflect the higher coverage of the alumina surface by tetrahedral tungstate entities (*41*).

The activation of the hexavalent molybdate precursor may be described by analogy with that of the corresponding tungstate entities (*21*): The thermal treatment effects a desorption of molecules and surface groups, which may block the coordination sites of the Mo(VI) species. OH groups in the vicinity of the Mo(VI) sites are assumed to play the key role. Their stability against desorption should be increased by their interaction with the Mo species, in particular if the latter are isolated. On the other hand, their removal should be facilitated if the Mo species become neighbors themselves. Thus, the increase of the required temperatures with decreasing MoO_3 content could be explained.

The mechanism of carbene formation from the hexavalent precursors remains to be elucidated in the future. A possible route was proposed earlier by Rappe and Goddard (*20*):



This route has recently been verified for the photocatalytic propene metathesis (*17*).

It may be speculated that the decrease in activity observed after the application of too high activation temperatures is due to a growing extent of the thermal reduction of Mo(VI) species. We do not stress this view as other processes (formation of $Al_2(MoO_4)_3$ and sublimation of MoO_3) may proceed in the same temperature range.

2. Activation by reduction in hydrogen. In view of the complexity of reduced MoO_3/Al_2O_3 surfaces reduced at temperatures of ≈800 K (Mo(VI), Mo(V), Mo(IV)—isolated or paired, and Mo(II) coexisting), it seems to be fruitless to look for any correlation between the quantity of a particular state and the metathesis activity. However, the material summarized in Figs. 5 and 6 contains information allowing at least qualitative assignments.

With the Mo13 catalyst (Fig. 6) four Mo states can be discerned from their influence on the metathesis activity in a temperature range where Mo(0) has not yet been formed ($T_{red} \leq 823$ K). The first (active) one works in the thermally activated sample. Its activity is indicated by the shaded region in Fig. 6. The reduction leads to an increase in activity, presumably due to the formation of additional active site precursors (vide infra). However, this increase is delayed as can be seen in the curves for $T_{red} = 673$ and 773 K. Obviously, an inactive Mo state precedes the second active Mo state in the course of the reduction. Moreover, the Mo state following this second active one is also inactive, because the activity decays again with increasing reduction extent. With the Mo states shown by XPS to be present on the surface of reduced MoO_3/Al_2O_3 (*23*), the following sequence describing the relevance of Mo states as active site precursors can be set up:

$$\mathrm{Mo(VI)_{active}} \rightarrow \mathrm{Mo(V)_{inactive}} \rightarrow \mathrm{Mo(IV)_{is(active)}} \rightarrow [\mathrm{Mo(II)\ and\ Mo(IV)_{pairs}}]_{\mathrm{inactive}}. \quad (3)$$

From the development of the activity at 900 and 973 K (Figs. 5 and 6) it can be concluded that metallic molybdenum does not form metathesis sites either. Hence, by analogy with the WO_3/Al_2O_3 system (*21*) we find both Mo(VI) and isolated Mo(IV) ($\mathrm{Mo(IV)_{is}}$) to be potential precursors of the metathesis sites. Possible routes of carbene formation from Mo(IV) precursors have been discussed in the literature (*2*, *5*).

Equation (3) is not intended to mean that all species of the given valency are relevant for the metathesis reaction. The insignificant loss of activity within the first 40 min of the reduction at 673 K (Fig. 6) suggests rather that the reduction first attacks Mo(VI) species not involved in the formation of active sites. It may, of course, be argued that the constant activity level may originate from a 1 : 1 interconversion between Mo(VI) and Mo(V) precursors of sites of equal activity. This would imply, however, that the precursor species include the most reducible Mo(VI) entities. The observation that the largest TOF are exhibited by the catalysts with the lowest reducibility (Fig. 2) does not favor this view. Accordingly, the increase in metathesis activity following the first 40-min period in the reduction at 673 K should not result from a conversion of Mo(VI) precursor species into Mo(IV) precursors, which would then produce sites of higher intrinsic activity. More likely, additional precursors are formed from the more reducible molybdate structures.

This view is supported by an inspection of the response of Mo7 to the reductive activation (Fig. 5). If the Mo(VI) precursors were consumed in the first stages of the reduction we would expect a pattern similar to that in Fig. 6 except for a shift to higher reduction temperatures. This expectation is based on the observation that the development of the distribution between Mo(VI), Mo(V), and $\mathrm{Mo(IV)_{is}}$ with proceeding reduction of Mo7 roughly parallels that found with Mo13 at lower reduction temperatures, which provide differences in the Mo(II) and Mo(0) states not relevant to metathesis (*23*). The activity pattern is, however, quite different, which can be explained by the fact that the TOF obtained by thermal treatment is higher with Mo7 than with Mo13. Therefore, while the effects originating from the Mo states below +6 are clearly visible on the background of a low Mo(VI)-derived activity in the case of Mo13, they are nearly covered by the higher Mo(VI)-derived contribution with catalysts containing ≤7 wt% MoO_3.

It should be kept in mind that the activities discussed above can be observed only when the hydrogen retained on the catalyst surface is stripped off. They are lost when hydrogen is readsorbed at temperatures of about 800 K (Table 3). It has been shown that this readsorption of hydrogen does not restore the Mo state distribution obtained after the reduction (*23*). Hence, we believe that the hydrogen affects the metathesis activity by blocking the active sites rather than by changing Mo valencies (*42*). Remarkably, the chemisorbed hydrogen quenches the activity completely, i.e., including the Mo(VI)-derived contribution. This implies that it also interacts with the hexavalent precursors, which agrees with earlier observations with WO_3/Al_2O_3 catalysts (*21*).

CONCLUSIONS

MoO_3/Al_2O_3 catalysts can be activated for the metathesis of propene by thermal treatment in flowing inert gas. The activation temperatures required increase with decreasing Mo loading from 900 K (≃2.3 Mo atoms/nm^2) to 1140 K (≃0.1 Mo atoms/nm^2). The activity of the supported Mo (molecules s^{-1} Mo^{-1}) increases with decreasing Mo content; i.e., the trend is opposing that for the reducibility of these catalysts.

The kinetic reaction order of the propene metathesis over thermally activated MoO_3/Al_2O_3 was found to be 0.8 at 473 K. The apparent activation energy was 37–30 kJ/mole, decreasing slightly with increasing Mo content.

The metathesis activity has been investigated at different reduction states of the catalyst surface. It has been concluded that on the reduced surface active sites may be formed from coexisting Mo(VI) and Mo(IV) precursors while Mo(V), Mo(II), and Mo(0) do not contribute to the activity. The effect of the Mo(IV) precursor was most pronounced with a catalyst of high MoO_3 content, but partly covered by a higher Mo(VI)-derived activity contribution with catalysts of lower MoO_3 content. The activity of catalysts activated by mere thermal treatment in inert gas originates exclusively from active sites derived from Mo(VI) precursors.

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